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Impregnated carbon based catalyst for protection against carbon monoxide gas

Beer Singh *, Amit Saxena *, Avanish Kumar Srivastava, R. Vijayaraghavan

Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, MP, India

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ABSTRACT

Activated carbon based palladium impregnated catalyst (Pd/C) was prepared for the reactive removal of carbon monoxide (CO) gas under ambient air conditions. For this, active carbon of 1250 m^2/g surface area was impregnated with palladium salt to get Pd/C catalyst, containing palladium from 4.0 to 8.0% (w/w). Catalytic efficiency of the catalyst against CO gas was determined under dynamic conditions by passing CO–air mixture to the fixed bed of the Pd/C catalyst. Results indicated that Pd/C catalyst was continuously adsorbing and actively removing CO gas during the course of the palladium catalyzed reaction, i.e., $CO + 1/2\ O_2 \rightarrow CO_2$ and was found capable of providing excellent protection against CO gas. Moisture content (humidity) of inlet CO–air mixture indicated it to be an important factor affecting the CO removal efficiency of the catalyst, as an increase in humidity after the CO breakthrough resulted in to the activation of the catalyst due to the generation of hydroxyl groups and enhanced protection by the regeneration of the catalyst. Study indicated that Pd/C catalyst works as a catalytic converter, i.e., the continuous conversion of CO to CO_2 using atmospheric oxygen and moisture. In order to determine the shelf life, the Pd/C catalyst was also evaluated for its performance after accelerated ageing at 70 °C and 50% relative humidity (RH) for 3.75 and 7.5 months. The catalyst was found to be working efficiently for 3.75 months but after 7.5 months it could not provide 100% protection against CO gas, however, the same catalyst started giving 100% protection after regeneration. Hence, studies indicated the Pd/C catalyst to be a promising catalyst for the reactive removal of CO gas in enclosed spaces/compartments, coal mines, fire accidents and for getting the protection for longer duration under ambient air conditions.

1. Introduction

Carbon monoxide, a hemo-toxic chemical hazard is produced due to incomplete combustion of articles. Fires in enclosed spaces (a ship hold), gunfire (generally with high explosives), products from flamethrower and engine exhaust (particularly when rich mixtures are employed), etc., may give rise to dangerous concentrations of CO gas. Therefore, there is a great concern among the scientists to have protection against deadly toxic CO gas.

During World War-I the subject was investigated very widely [1]. As CO gas is very light, direct adsorption is apparently out of question. Permanent bonding of CO with hemoglobin indicates that synthetic analogue of hemoglobin may be a suitable material, if could be prepared. Direct blood is of no use. Several oxidants such as hoolamite (I_2O_5 + fuming H_2SO_4), silver permanganate, hopcalite, etc. were also developed [1]. Hopcalite was the most successful adsorbent, which is a mixture of MnO_2 and CuO. It utilizes the atmospheric air for the oxidation of CO gas. The hopcalite is a moisture sensitive catalyst and its catalytic activity is greatly reduced due to the presence of moisture in air. To save hopcalite from moisture the CO canister contains the desiccant layer/bed [1], which absorbs the moisture of the inlet CO contaminated air.

The efficiency and service life of hopcalite based CO canister mainly depends on the desiccant layer, i.e., as soon as the desiccant is saturated with moisture, it allows the moisture to come in contact with hopcalite layer and deactivates it. Therefore, the main disadvantage associated with hopcalite is it's poisoning due to water, which makes it to be unsuitable for longer duration or under humid conditions. Another disadvantage of hopcalite is its lesser shelf life and limited protection against CO gas. Therefore, in order to provide respiratory or collective protection against CO a suitable filtration system can be employed, which performs the catalytic oxidation of CO gas for removing it or at least minimizing its concentration. So far, most of effective catalysts for this system have been reported to use the supported noble metals such as Pt [2–4], Pd [4], Au [5], Ru [4,6,7] and Rh [8,9].

Oxides of platinum and gold, and ozone were also investigated for their efficiency for the oxidation of CO gas [10–14]. Many researchers have reported palladium as an efficient metal for the

* Corresponding author. Tel.: +91 751 2341960; fax: +91 751 2341148.
E-mail addresses: beerbs5@rediffmail.com (B. Singh), amsa888@rediffmail.com (A. Saxena).

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Table 1
Surface area and pore volumes of active carbon and 4–8% Pd/C catalyst.

S. no.	Catalyst systems	Palladium % (w/w)		Surface area (N_2 BET) (m^2/g)	Micropore volume (N_2 DR) (cm^3/g)	Cumulative pore volume (N_2 BJH) (cm^3/g)
		Theoretical	Extracted			
1	Active carbon	Nil	Nil	1250	0.742	0.409
2	Pd/C	4.0	3.81	1240	0.721	0.348
3	Pd/C	5.0	4.84	1232	0.732	0.346
4	Pd/C	5.5	5.30	1228	0.708	0.328
5	Pd/C	6.0	5.81	1230	0.718	0.310
6	Pd/C	6.5	6.28	1223	0.704	0.323
7	Pd/C	8.0	7.78	1198	0.688	0.316

oxidation of CO gas over metal oxides [15–17]. Adsorption and oxidation of CO on palladium has been discussed in detail by Matsushima et al. [18] and Zhang and Hu [19].

In last few years various catalysts [20–24] based on CuO/CeO_2, CuO_x–CeO_2–ZrO_2, CuO/Al_2O_3 were prepared and reported to be exhibiting catalytic activity similar to that of noble metal catalysts for the oxidation of CO gas, but their optimal reaction temperature is about 200 °C. Cobalt oxide was verified to be a good promoter for improving the catalytic activity of $CuO/CeO_2/Al_2O_3$ based catalyst for CO oxidation [24,25]. Literature also reveals the use of nanoparticles of silver, gold, silver–gold alloy and nickel ferrite for the catalytic removal of CO gas [26–29]. Suh et al. [30] discussed the promotional effect of surface oxygen groups on homogenous palladium dispersion.

Literature revels that no suitable adsorbent or catalyst for the removal of CO gas from air under ambient conditions is available. Therefore, the aim of the present study was to develop an excellent catalyst, which can be used at ambient conditions to remove CO gas.

2. Experimental

2.1. Materials/detectors

Active carbon, grade 80 CTC of 12× 30 BSS particle size, coconut shell origin and 1250 m^2/g surface area (N_2-BET) was obtained from M/s Active Carbon India Ltd., Hyderabad, India. CO gas cylinder used was from M/s Inox Air Products, Mumbai, India. Detectors used for the detection of CO and CO_2 gas were microprocessor-based Personal Analyzer Model SR-2000 (CO detection limit 0–2000 ppm and resolution 1 ppm) and IR-based portable Carbon Dioxide Gas Analyzer Model P-CO_2-89 (CO_2 detection limit 0–10000 ppm and resolution 2 ppm), respectively from M/s Technovation Analytical Instruments Pvt. Ltd., Mumbai, India.

2.2. Preparation and characterization of catalysts (Pd/C)

Different Pd/C catalyst samples having palladium content from 4.0 to 8.0% (w/w) were prepared [31,32]. In order to prepare Pd/C catalyst, coconut shell based granular activated carbon, grade 80 CTC, particle size 12× 30 BSS and surface area 1250 m^2/g was taken. Initially, 100 g granular activated carbon was allowed to react with 500 mL of 10% nitric acid at 60 °C for 8 h to generate acidic surface functional groups. After acid treatment the carbon was washed with deionized water till it became neutral (pH ~ 7). Finally it was dried in an oven at 110 °C for 4 h, cooled in desiccators and kept in airtight bottles for further processing.

For 6.5% palladium impregnated catalyst, 24.0 g so produced acidic group functionalized carbon was poured to 300 mL of distilled water and heated at 80 °C for 5 min. To this, a solution of 2.78 g of palladium chloride (as per required percentage of impregnation) in 7.0 mL of concentrated hydrochloric acid and 16.0 mL of distilled water was added. The solution was continuously stirred for 5 min. To this 25.0 mL of 37% formaldehyde solution was added and the solution was made slightly alkaline (pH ~ 8) using 30% sodium hydroxide solution. The suspension was continuously stirred for 20 min. The material was then filtered, cooled and washed 10 times with 100 mL portion of distilled water. The material was dried in an oven at 80 °C for 12 h and then in desiccators over potassium hydroxide. Finally the material (6.5% Pd/C) was stored in airtight bottles till further use. All catalytic systems (4.0–8.0% palladium, w/w) were synthesized using the similar experimental conditions and corresponding amount of chemicals. In order to find out the actual palladium loadings, palladium was extracted from palladium impregnated carbon using aqua regia and the concentration of palladium was determined using Atomic Absorption Spectrophotometer [33]. Results indicated the palladium content to be >95% of theoretical loadings (Table 1).

Moisture content of the catalytic systems was determined using ASTM method (D 2867-83) which was found to be in the range from 3.5 to 4.2%.

Before studying Pd/C catalyst for the catalytic removal of CO gas, prepared catalyst samples were characterized for surface area (N_2-BET method), micropore volume (N_2-DR method) and cumulative pore volume (N_2-BJH method) at 77 K by nitrogen adsorption at liquid nitrogen temperature using Autosorb 1C from Quanta chrome, USA. Figs. 1 and 2 and Table 1 represents the results.

2.3. Test-rig for the catalytic removal of CO gas over Pd/C catalyst

Fig. 3 shows the test-rig used to generate CO–air mixture of different concentrations and determine the efficiency of prepared Pd/C catalysts against CO gas. CO was taken from CO gas cylinder (1) at required flow rate using control valve (2) and flow meter (3),

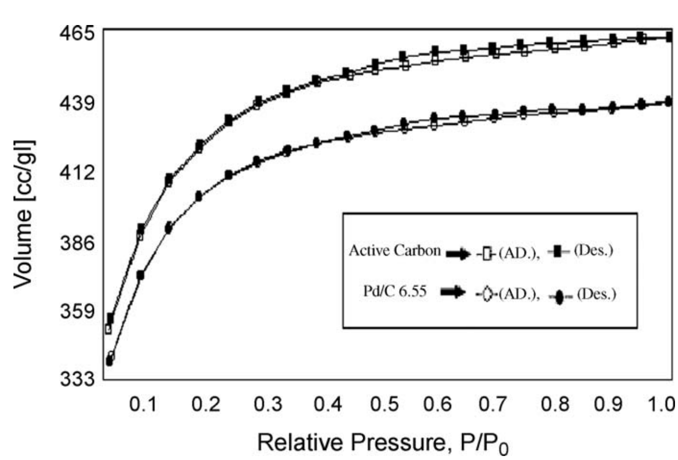

Fig. 1. Adsorption–desorption isotherm of active carbon and Pd/C (6.5% Pd, w/w) catalyst.

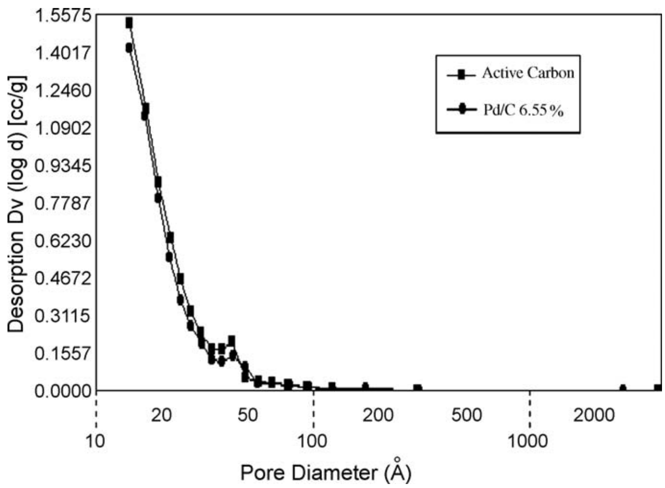

Fig. 2. BJH pore size distribution curve of active carbon and Pd/C (6.5% Pd, w/w) catalyst.

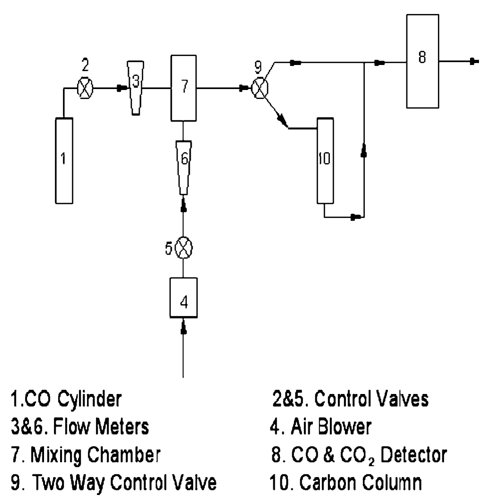

Fig. 3. Schematic of the test-rig for the evaluation of Pd/C catalyst against CO gas.

which was mixed with ambient air, taken through air blower (4) using control valve (5) and flow meter (6) in a mixing chamber (7). The concentration of CO–air mixture, thus produced was determined by passing it to CO detector (8) using two-way control valve (9). Having determined the CO concentration, CO–air mixture was then passed through the Pd/C column (10) using two-way control valve (9) and the CO breakthrough time (CO btt) was monitored by passing the column outlet to the CO detector (8). CO_2 outlet concentration was also determined simultaneously by passing the column outlet to CO_2 detector (8).

Table 2
Experimental conditions.

Parameter	Values
Bed height of carbon	5.0 cm
Column diameter	2.0 cm
CO–air mixture flow rate	4.5 Lpm[a]
CO inlet concentration	131 ppm (150 mg/M^3)
Temperature	30 ± 1 °C
Relative humidity	50 ± 5% or nil (0.2%)

[a]Airflow rate in miniaturized filter in form of a carbon column = cross-sectional area of carbon column × air velocity corresponding to the filter with 200 M^3/h air filtration capacity = 3.14 cm^2 × 23.9 cm/s = 4.50 Lpm (liters per minute).

Table 3
Effect of palladium concentrations on CO breakthrough behavior at 131 ppm of CO inlet concentration.

Time (min)	Outlet concentration of CO gas (ppm) through Pd/C with					
	4.0% Pd	5.0% Pd	5.5% Pd	6.0% Pd	6.5% Pd	8.0% Pd
1	0	0	0	0	0	0
2	12	2	1	0	0	0
10	15	3	0	0	0	0
25	15	4	2	0	0	0
60	15	3	1	0	0	0
240	16	3	1	0	0	0
400	15	4	2	0	0	0

Pd/C catalyst was to be used for filtering the CO contaminated air at 200 M^3/h flow rate (air velocity = 23.9 cm/s) and 150 mg/M^3 CO inlet concentration. For that, before the use of Pd/C catalyst in filter, it was, therefore, evaluated using a miniaturized filter in form of a carbon column of same bed height, i.e., 5.0 cm at the air velocity, corresponding to air filter of 200 M^3/h capacity, i.e., 23.9 cm/s. Overall experimental conditions have been tabulated in Table 2. The catalyst was also tested at higher concentrations of CO gas (up to 655 ppm). Tables 3–6 represent the effect of Pd, CO, CO_2 conversion and RH.

2.4. Accelerated ageing study of Pd/C catalyst

In order to check the suitability of the catalyst for longer duration storage, the accelerated ageing of the catalyst was carried out by storing it at 70 °C and 50% RH for 3.75 and 7.5 months in desiccators.

2.5. Regeneration of Pd/C catalyst

For the regeneration of aged Pd/C, a known weight (25.0 g) of the catalyst (6.5% Pd/C) was poured to 75 mL of distilled water followed by the addition of 25.0 mL of 37% formaldehyde solution with continuous stirring. The solution was made slightly alkaline

Table 4
Effect of increase in CO inlet concentration on breakthrough behavior of Pd/C with different percentages of palladium.

Time (min)	Outlet concentration of CO gas (ppm) through Pd/C with							
	5.0% Pd	5.5% Pd		6.5% Pd			8.0% Pd	
	At 262 ppm of CO inlet conc.	At 262 ppm of CO inlet conc.	At 655 ppm of CO inlet conc.	At 262 ppm of CO inlet conc.	At 393 ppm of CO inlet conc.	At 655 ppm of CO inlet conc.	At 262 ppm of CO inlet conc.	At 655 ppm of CO inlet conc.
1	4	3	22	1	6	20	0	0
5	24	1	47	3	10	42	0	0
12	26	1	88	3	10	78	0	0
18	26	4	85	3	12	80	0	0
60	28	5	88	4	12	80	0	0
240	30	5	90	4	12	82	0	0
400	28	4	89	5	13	81	0	0

Table 5
Quantitative data of CO_2 at different CO inlet concentration over Pd/C.

CO inlet (ppm)	CO outlet (ppm)	CO_2 inlet (ppm)	CO_2 outlet (ppm)
131	00	300	400
265	00	300	500
575	00	300	750

Table 6
Effect of atmospheric moisture on CO breakthrough behavior in Pd/C (6.5% Pd, w/w) catalyst at 131 ppm of CO inlet concentration.

Time (min)	Outlet concentration (ppm) (air from cylinder, RH ~nil (0.2%))	Outlet concentration (ppm) (air, RH ~55%)
1	0	0
50	0	0
55	4	0
65	13	0
68	24	0
70	32	0
75	48	0
400	–	0

using 30% sodium hydroxide solution. The suspension was continuously stirred for 30 min. The material was then filtered, cooled and washed 10 times with 100 mL portion of distilled water. The material was dried in an oven at 80 °C for 12 h and then in desiccators over potassium hydroxide [31]. Pd/C catalyst, thus regenerated was further evaluated under similar experimental conditions against CO gas (Table 7).

3. Results and discussion

3.1. Effect of palladium concentration

Active carbon of surface area 1250 m^2/g when was impregnated with palladium showed a small decrease in surface area and pore volume [34,35] (Table 1). It was due to the impregnant, which sit in the mesopores and the pore openings of micropores. The samples exhibited hysteresis loop, which is the characteristic of adsorption possessing a portion of mesopores with mesopore maxima at ~22 Å. All samples of Pd/C catalyst gave comparable value of their surface area and pore volumes (Table 1) and influenced a very little with percentage of impregnation. Fig. 1 showed the adsorption and desorption pattern of active carbon and 6.5% Palladium impregnated carbon (Pd/C). Active carbon and palladium impregnated carbon showed the micropore maxima at 14.33 and 14.16 Å, and mesopore maxima at 21.87 and 21.88 Å, respectively. Pore maxima and Fig. 2 clearly indicated that active carbon and palladium-impregnated carbon have more or less similar type of BJH pore size distributions. Due to higher surface area and micropore volume (Table 1) Pd/C catalyst might provide more contact time than hoolamite, silver permanganate and hopcalite [1] to CO molecules to interact with palladium available on the surface of the Pd/C, however, the percentage of catalytic reaction will depend on amount of palladium loaded on the surface of active carbon.

In order to understand the effect of palladium concentration on Pd/C against CO gas various samples with different percentages of palladium content were evaluated for CO gas removal efficiency under the set of experimental conditions (Table 2) [36]. Table 3 describes the CO breakthrough behavior with these catalysts. 4.0% palladium impregnated carbon catalyst could not remove CO gas completely and showed outlet concentration of 15 ppm of CO after 10 min, i.e., the breakthrough time is less than 10 min. Interesting observation was that the Pd/C catalyst did not show any increase in CO concentration after 10 min and showed same value of out let concentration, i.e., 15 ppm till the experiment was conducted, i.e., up to 400 min. 5.0 and 5.5% Pd/C catalyst showed good results and could remove 97 and 98% of 131 ppm of CO gas, respectively. However, 6.0, 6.5 and 8.0% Pd/C catalysts did not show any breakthrough of CO gas till the experiment was continued, i.e., 400 min. This indicated that palladium more than 6.0% in Pd/C catalytic system is sufficient for CO gas removal and to be on safer side it can be described that 6.5% palladium impregnated carbon catalyst is the optimized one for continuously removing CO gas under the studied conditions. The catalysts showed very high protection against CO gas under ambient conditions and were found to be working as a real turn over catalyst. The constant value of CO outlet concentration (Table 3) indicated that the Pd/C catalyst works as a catalytic converter, i.e., the continuous conversion of CO to CO_2 using atmospheric oxygen. Study also indicated that active carbon without palladium does not show any protection against 131 ppm of carbon monoxide gas.

3.2. Effect of CO concentration

Table 4 describes the effect of CO concentration on breakthrough behavior with the studied catalysts. In order to increase the CO concentration and maintain the same flow rate of CO–air mixture the flow meters of CO cylinder and ambient air were adjusted accordingly. Pd/C catalyst containing 5.0% palladium did not show good protection at double concentration of CO gas, i.e., at 262 ppm. As this catalyst was removing 97% of CO gas at 131 ppm but when the concentration of CO is doubled it could remove 90% only. Pd/C catalyst containing 5.5% palladium showed promising protection at 262 ppm but when the concentration of CO was increased to 655 ppm it could remove only 87% of CO after an equilibration time of 12 min. The catalyst with optimum 6.5% palladium in Pd/C showed good results up to 363 ppm of CO, however, this also could remove 88% of CO at 655 ppm CO inlet concentration after an equilibration time of 12 min. It indicated that 6.5% palladium impregnated carbon catalyst is the best with a factor of safety 2 under given set of experimental conditions. 8.0% palladium impregnated carbon catalyst did not show any breakthrough of CO gas even if the concentration was increased to

Table 7
Effect of accelerated ageing and regeneration on Pd/C (6.5% Pd, w/w) catalyst.

Time (min)	Outlet concentration of CO (ppm)					
	Before ageing		After ageing ~3.75 months		After ageing ~7.5 months	Regenerated Pd/C[a]
	At 131 ppm of CO inlet conc.	At 262 ppm of CO inlet conc.	At 131 ppm of CO inlet conc.	At 262 ppm of CO inlet conc.	At 131 ppm of CO inlet conc.	At 131 ppm of CO inlet conc.
1	0	1	0	10	10	0
5	0	3	0	7	18	0
60	0	4	0	6	38	0
200	0	3	0	6	58	0
400	0	4	0	8	–	0

[a] Pertain to regeneration of 7.5 months old (under 70 °C and 50% RH) Pd/C.

655 ppm. Table 5 indicates the formation of CO_2 due to the reaction of CO gas with palladium over Pd/C catalyst, and represents a quantitative data of CO_2 at different CO inlet concentration over 8.0% Pd/C.

3.3. Effect of humidity

Table 6 depicts the effect of humidity on CO adsorption potential of Pd/C catalyst with 6.5% Pd (w/w). When the air for the dilution of CO gas was taken from air cylinder having nil (~0.2%) moisture content the breakthrough behavior of CO gas was very interesting. Up to 50 min CO outlet concentration was nil, at 55 min it was 4 ppm and at 65 min it was 13 ppm. At 75 min the outlet CO concentration was 48 ppm, which indicated a fast breakthrough of CO gas. The outlet CO concentration increased suddenly after 50 min under no moisture conditions because the moisture present in palladium impregnated carbon got exhausted. Desorption of water, facilitated the deactivation of the catalyst by the self-elevated temperature of the catalyst due to exothermic CO oxidation, indicating that probably the catalyst functions efficiently provided it consists of the optimum moisture content, the same has been reported by Date and Haruta [37].

When ambient air having 55% RH was taken for the dilution of CO gas, the outlet concentration of CO gas remained nil throughout the experiment, i.e., up to 400 min. It highlighted the necessity of moisture for the effective removal of CO gas, as the RH of the air could maintain the required moisture content and thus did not allow the deactivation of the catalyst due to desorption of water.

In order to confirm the necessity of moisture, more experiments were conducted. In one of the experiment initially air of 0.2% RH (air from air cylinder) was used to dilute CO gas for CO btt studies on Pd/C catalyst. At 65 min the outlet concentration of CO gas was 13 ppm, which increased to 48 ppm at 75 min. Deactivation of the catalyst due to its dehydration was found to be reversible. Reversibility was verified by replacing the air cylinder with one ambient air pump to take atmospheric air with higher RH and on the day of experiment RH was 55%. The outlet concentration of CO gas started coming down and within minute it reached to nil. Thus exposure of the deactivated catalyst with humid air provided the recovery of the deactivated catalyst. Deactivation of the catalyst was clearly synchronized with the end of the catalyst dehydration process.

3.4. Mechanism of reaction and regeneration/reproducibility

Reactions (1)–(3) describes the probable mechanism for the catalytic conversion of CO to CO_2 over the surface of palladium impregnated carbon catalyst [38,39] and the regeneration of the catalyst by atmospheric water [40]. Pd/C catalyst initially adsorbs CO gas then it converts CO to CO_2 by utilizing atmospheric oxygen [14]. The formation of CO_2 was confirmed by passing the column outlet gas to CO_2 detector, indicating the presence of CO_2 in the outlet stream (Table 5). When air from air cylinder (RH ~ 0.2%) was used for the dilution of CO gas, desorption of water, facilitated the deactivation of the catalyst by the self-elevated temperature of the catalyst due to exothermic CO oxidation (Table 6). Table 6 indicates that probably the catalyst functions efficiently provided it consists of the optimum moisture content as the increase in RH from 0.2 to 55% could regenerate the catalyst. This was evidenced due to a decrease in CO outlet concentration (Table 6).

Water from air streams of higher RH can also be adsorbed and held over the surface of the catalyst, and can block active sites, however, simultaneous desorption of water facilitated by the self-elevated temperature due to exothermic CO oxidation, accompanied this non-heated catalysis. In that fashion, the catalyst (Pd/C) gets regenerated [40] and provides excellent protection against CO gas. This phenomenon of regeneration of the catalyst makes Pd/C catalyst to be the best one for CO gas removal under ambient conditions of temperature and humidity. Activation of catalyst by water molecules after an increase in RH was thought to be following either through the path of removal of CO_2 already adsorbed during the course of CO oxidation on the active sites of catalyst or via the replenishing/regenerating the hydroxyl groups on the surface of the support of the catalyst, i.e., carbon.

In order to investigate the deactivation and activation of the palladium impregnated carbon, adsorption and desorption of CO_2 were studied for active carbon and the catalyst, i.e., palladium impregnated carbon using 5400 ppm carbon dioxide inlet concentration. The experimental conditions have been kept same as that of CO breakthrough study (Table 2). The study indicated no adsorption of CO_2 by both the systems as the outlet showed the same inlet concentration, i.e., 5400 within a minute of exposure. This behavior of CO_2 desorption is consistent with that discussed in the literature [41]. So the possibility of the deactivation via blocking of the active sites of the catalyst by carbon dioxide and preventing further adsorption of carbon monoxide is overruled and so also the activation of the catalyst via the path of removal of CO_2 already adsorbed on the active sites of catalyst during the course of CO oxidation by water molecules is overruled. Therefore, activation of the catalyst via regeneration of the hydroxyl groups on the surface of the support of the catalyst, i.e., carbon, seems to be appropriate.

The critical role of water in the activation of the catalyst via the surface hydroxyl groups is found consistent with that discussed by Schryer et al. [38] and Liang et al. [39]. During the course of the reaction the concentration of the hydroxyl groups gets depleted due to their consumption in CO removal and the dehydration of the catalyst owing to the exothermic CO oxidation resulted in the decline in catalyst activity.

If the hydroxyl group concentration at the catalyst surface is restored by humidification of the reaction gas mixture, deactivated catalyst is found to be activated. Humidification of the catalyst surface may increase the hydroxyl group concentration to the optimum value and the activity of the catalyst may then be enhanced [37].

Participation of the hydroxyl groups in the CO oxidation has already been reported by Liang et al. [39], Mhadeshwar and Vlachos [42] and Bergald et al. [43]. The formation of hydroxyl group on the surface of palladium has also been reported by Cao and Chen [44] and Wolf et al. [45]. The literature [39,42–45] indicates the formation of hydroxyl groups promoted by water through the following reaction:

$$H_2O + O* \rightarrow 2OH* \quad (1)$$

On the basis of the above reported studies, H_2O may participate in the CO oxidation via the reaction between CO and OH groups and following reaction pathways are then proposed for CO oxidation over palladium impregnated carbon:

$$H_2O + O* \rightarrow 2OH* \quad (1)$$

$$Pd{-}CO + OH* \rightarrow Pd + CO_2 + H* \quad (2)$$

$$H* + O* \rightarrow OH* + _* \quad (3)$$

$$H* + OH* \rightarrow H_2O* + _* \quad (4)$$

where suffix '*' denotes an empty site or an adsorbed species.

H* is formed, which cannot combine together to release H_2 at current conditions due to the large amount of O_2 in the stream. Instead of that, Hs may react with oxygen to liberate H_2O [39].

The sum of the reactions (1)+(2)+(3)+(4), yields the overall reaction

$$Pd{-}CO + O* \rightarrow Pd + CO_2 \quad (5)$$

As a whole, the presence of H_2O can supply abundant OH groups in the presence of O_2, and then OH groups react with the adsorbed CO on Pd species to produce CO_2 as per reaction (2) and it is consistent with that discussed in the literature [39,42,43].

3.5. Accelerated ageing study

After ageing treatment the catalyst was re-evaluated for its efficiency against CO gas. Table 7 represents the behavior of Pd/C catalyst containing theoretically 6.5% (w/w) palladium before and after ageing against 131 and 262 ppm of CO inlet concentration. It indicated that the catalyst after 3.75 months of ageing gave same protection against 131 ppm and slightly lower against 262 ppm of CO inlet concentration. The Pd/C catalyst after 7.5 months of ageing did not show promising results against 131 ppm of CO inlet concentration and the outlet concentration of CO gas increased from 10 to 58 within 200 min. Pd/C being the costly catalyst, the suitability of the catalyst for its regeneration/reproduction capability after deactivation due to storage was also explored. The deactivation of Pd/C catalyst on longer duration of storage was probably due to the conversion of palladium to palladium salts such as palladium oxide.

3.6. Regeneration of Pd/C after ageing of 7.5 months

When, regenerated Pd/C with theoretically 6.5% (w/w) palladium was further evaluated under same experimental conditions against CO gas (Table 7), it showed excellent protection, i.e., zero CO outlet concentration. This indicated that the Pd/C catalyst can be regenerated easily at a very low cost and can be reused.

It can be inferred from the study that 6.5% (actual 6.28%) palladium impregnated carbon based catalyst is suitable enough to provide protection against CO gas for longer duration under the set of given conditions. The developed catalyst can be used in filters for protection against CO gas in enclosed chambers. This catalyst can also be used in canisters for individual protection against CO gas in enclosed areas such as coal mines and during fire accidents or in open.

4. Conclusion

Samples of Pd/C catalyst containing theoretically 4.0, 5.0, 5.5, 6.0 6.5 and 8.0% (w/w) palladium on active carbon were prepared for the catalytic removal of carbon monoxide gas under ambient conditions. Optimum content of palladium in Pd/C was found to be 6.5% (theoretical, as per extraction 6.28%) for providing excellent protection against CO gas. The catalyst was found to be working as a catalytic converter, i.e., the continuous conversion of CO to CO_2 using atmospheric oxygen. Study also indicated that the moisture content of CO–air mixture helps in regeneration of Pd/C catalyst and promotes the CO oxidation. The Pd/C catalyst after accelerated ageing for 3.75 months was found to be working efficiently but after 7.5 months it could not provide 100% protection against CO gas, however, the same catalyst started giving required (100%) protection after regeneration. Therefore, it can be concluded from the study that the developed and evaluated Pd/C catalyst is a promising catalyst material for use in filters and canisters to achieve protection against deadly toxic CO gas in coal mines, fire accidents and in enclosed spaces/chambers.

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References

[1] W.A. Noyes Jr., Summary Technical report of the National Defence Research Committee Division 10, Washington, DC (1946).
[2] M. Watanabe, H. Uchida, K. Ohkubo, H. Igarashi, Appl. Catal. B 46 (2003) 600–611.
[3] Ş. Özkara, A.E. Aksoylu, Appl. Catal. A 251 (2003) 75–83.
[4] P.V. Snytnikov, V.A. Sobyanin, V.D. Belyaev, P.G. Tsyrulnikov, N.B. Shitova, D.A. Shlyapin, Appl. Catal. A 239 (2003) 149–156.
[5] R.J.H. Grisel, C.J. Weststrate, A. Goossens, M.W.J. Craje, A.M. Kraan, B.E. Nieuwenhuys, Catal. Today 72 (2002) 123–132.
[6] A. Worner, C. Friedrich, R. Tamme, Appl. Catal. A 245 (2003) 1–14.
[7] R.M.T. Sanchez, A. Ueda, K. Tanaka, M. Haruta, J. Catal. 168 (1997) 125–127.
[8] G.W. Chen, Q. Yuan, H.Q. Li, S. Li, Chem. Eng. J. 101 (2004) 101–106.
[9] H. Tanaka, S.I. Ito, S. Kameoka, K. Kunimiori, Catal. Commun. 4 (2003) 1–4.
[10] V. Yakhnin, M. Menzinger, Chem. Eng. Sci. 61 (2006) 347–352.
[11] O. Pozdnyakova, D. Teschner, A. Wootsch, J. Krohnert, B. Steinhauer, H. Sauer, L. Toth, F.C. Jentoft, A.K. Gericke, Z. Paal, R. Schlogl, J. Catal. 237 (2006) 1–16.
[12] W.C. Li, M. Comotti, F. Schuth, J. Catal. 237 (2006) 190–196.
[13] B.K. Chang, B.W. Jang, S. Dai, S.H. Overbury, J. Catal. 236 (2005) 392–400.
[14] P. Konova, M. Stoyanova, A. Naydenov, St. Christoskova, D. Mehandjiev, Appl. Catal. A 298 (2006) 109–114.
[15] S. Abbet, A.M. Ferrari, L. Giordano, G. Pacchioni, H. Hakkinen, U. Landman, U. Heiz, Surf. Sci. 514 (2002) 249–255.
[16] F. Zhang, J. Chen, X. Zhang, W. Gao, R. Jin, N. Guan, Catal. Today 645 (2004) 93–95.
[17] O. Pozdnyakova, D. Teschner, A. Wootsch, J. Krohnert, B. Steinhauer, H. Sauer, L. Toth, F.C. Jentoft, A.K. Gericke, Z. Paal, R. Schlogl, J. Catal. 237 (2006) 17–28.
[18] T. Matsushima, C.J. Mussett, J.M. White, J. Catal. 41 (1976) 397–404.
[19] C.J. Zhang, P. Hu, J. Am. Chem. Soc. 123 (2001) 1166–1172.
[20] X. Zheng, X. Zhang, X. Wang, S. Wang, S. Wu, Appl. Catal. A 295 (2005) 142–149.
[21] M. Manzoli, R. Di Monte, F. Boccuzzi, S. Coluccia, J. Kaspar, Appl. Catal. B 61 (2005) 192–205.
[22] J.W. Park, J.H. Jeong, W.L. Yoon, H. Jung, H.T. Lee, D.K. Lee, Y.K. Park, Y.W. Rhee, Appl. Catal. A 274 (2004) 25–32.
[23] J.W. Park, J.H. Jeong, W.L. Yoon, C.S. Kim, D.K. Lee, Y.K. Park, Y.W. Rhee, Int. J. Hydrogen Energy 30 (2005) 209–220.
[24] J.W. Park, J.H. Jeong, W.L. Yoon, Y.W. Rhee, J. Power Sources 132 (2004) 18–28.
[25] P. Thormahlen, M. Skoglundh, E. Frideel, B. Andersson, J. Catal. 188 (1999) 300–310.
[26] D.C. Lim, I.L. Salido, Y.D. Kim, Surf. Sci. 598 (2005) 96–103.
[27] A. Wang, Y.P. Hsieh, Y.F. Chen, C.Y. Mou, J. Catal. 237 (2006) 197–206.
[28] M.M. Rashad, O.A. Fouad, Mater. Chem. Phys. 94 (2005) 365–370.
[29] W.B. Kim, G.J. Rodriguez-Rivera, S.T. Evans, T. Voitl, J.J. Einspahr, P.M. Voyles, J.A. Dumesic, J. Catal. 235 (2005) 327–332.
[30] D.J. Suh, T.J. Park, S.K. Ihm, Carbon 31 (1993) 427–435.
[31] B. Singh, A. Saxena, K. Sekhar, Palladium impregnated carbon system for the removal of carbon monoxide gas, filed for Indian Patent/2409/DEL/2006.
[32] A. Saxena, A.K Srivastava, B. Singh, K. Sekhar, An efficient catalyst for the removal of carbon monoxide and the process there of, filed for Indian Patent/2130/DEL/2007.
[33] J. Karthikeyan, P. Parameshwara, A.N. Shetty, P. Shetty, Indian J. Chem. Technol. 15 (2008) 186–189.
[34] R.C. Everson, E.T. Woodburn, A.R.M. Kirk, J. Catal. 58 (1979) 95–107.
[35] R.S. Dixit, L.L. Tavlarides, Ind. Eng. Chem. Process Des. Dev. 22 (1983) 1–9.
[36] J.A. Mieth, Schwarz, A. James, J. Catal. 118 (1989) 203–217.
[37] M. Date, M. Haruta, J. Catal. 201 (2001) 221–224.
[38] D.R. Schryer, B.T. Upchurch, B.D. Sidney, K.G. Brown, G.B. Hoflund, R.K. Herz, J. Catal. 130 (1991) 314–317.
[39] F. Liang, H. Zhu, Z. Qin, H. Wang, J. Wang, Catal. Lett. DOI:10.1007/s 10562-008-9630-2.
[40] A.J. Dyakonov, Appl. Catal. B Environ. 45 (2003) 257–267.
[41] H.J. Freud, M.W. Roberts, Surf. Sci. Report 25 (1996) 225–273.
[42] A.B. Mhadeshwar, D.G. Vlachos, J. Phys. Chem. B 108 (2004) 15246–15258.
[43] J. Bergald, B. Kasemo, D.V. Chakarov, Surf. Sci. 495 (2001) 815–820.
[44] Y. Cao, Z.-X. Chen, Surf. Sci. 600 (2001) 4572–4583.
[45] M. Wolf, S. Nettesheim, J.M. White, E. Hasselbrink, G. Ertl, J. Phys. Chem. 95 (1991) 4609–4619.